QUALITATIVE FEATURE OF THE LOW-LYING SPECTRUM OF INTRASHELL STATES OF 4-VALENCE-ELECTRON ATOMS DERIVED FROM SYMMETRY CONSIDERATION

C.G.Bao

Department of Physics, Zhongshan University, Guangzhou,510275,PRC

ABSTRACT: Inherent nodal surfaces existing in the wavefunctions of intrashell states of 4-valence-electron atoms have been investigated. The decisive effect of these surfaces has been demonstrated, the ordering of low-lying levels has been predicted, and a primary classification scheme has been proposed

PACS: 31.15.Hz, 03.65.-w, 31.90.+s, 31.50.+w

KEYWORDS: 4-electron atoms, symmetry consideration, classification of states, energy spectrum

The important role of symmetry in nature is well known. A number of laws (or constraints) based on symmetry have been discovered, they govern the evolution of basic physical processes in nature [1-5]. In quantum mechanical systems, owing to the invariance of the Hamiltonian with respect to symmetric operations (rotation, space inversion, particle permutation, etc.), the eigenstates are classified according to a set of quantum numbers , these numbers specify the transformation property of the wavefunctions under symmetric operations. Since an eigenstate must have a specific transformation property, the distribution of wavefunctions in coordinate space may be greatly constrained. It was found in [6-8] that the constraint is embodied by the existence of a special type of nodal surfaces, the so called inherent nodal surface (INS). In this paper, we shall demonstrate how the INS affect the spatial distributions of the wavefunctions of 4-electron atoms, and how the low-lying spectrum is thereby decisively affected.

Let us first study the origin of the INS in a general way. Let A be a point in a multi-dimensional coordinate space. Evidently, A is associated with a geometric configuration. Let O_i be a combined symmetric operation. In some cases, one may find a set of O_i (i =1 to m) to leave A invariant; i.e., $O_i A = A$ (For example, is the case of a 4-body system an equilateral tetrahedron configuration (ETH) is invariant to the rotation about a 2-fold axis together with two interchanges of the particles, refer to Fig.1). Let Ψ be an eigenstate. Let $\hat{O}_i$ be the operator acting on Ψ so that $\hat{O}_i \Psi(A) = \Psi(O_i A)$. When A is invariant to O_i , we have

$$\hat{O}_i \Psi(A) = \Psi(A). \qquad \text{(i = 1 to m)} \tag{1}$$

Owing to the inherent transformation property of Ψ, eq.(1) always can be written in matrix forms (as we shall see). In this form we have m sets of homogeneous linear algebra equations. These equations impose a very strong constraint on Ψ. Since a set of homogeneous equations does not always have non-zero solutions, in some cases Ψ must be zero at A. This is the origin of the INS. In the follows we shall concern mainly the 4-electron atomic systems, however the generalization to other quantum systems is straight forward.

An important geometric configuration with the strongest geometric symmetry for the 4-body systems is the equilateral tetrahedron (ETH). Let p_{ij} denotes an interchange of i and j. Let k' be a 2-fold axis of an ETH so that a rotation of the ETH about k' is equivalent to $p_{12}p_{34}$. Let i' be an axis originating from the nucleus vertical to k' and parallel to $\vec{r_2} - \vec{r_1}$, where $\vec{r_i}$ is the position vector of the i-th electron originating from the nucleus. . Let R^n_δ be an operator of rotation about the n-axis by δ (in degree), let P be the operator of a space inversion. One can prove that the ETH is invariant to

$$O_a = p(1423) P R^{k'}_{90} \tag{2}$$

$$O_b = p_{12} P R^{i'}_{180} \tag{3}$$

$$O_c = p(243) R^{\hat{r_1}}_{120} \tag{4}$$

where $p(1423)$ and $p(243)$ denote cyclic permutations, $\hat{r_1}$ is a unit vector along $\vec{r_1}$. There are other operators leave the ETH also invariant, e.g., the $p(134)R^{\hat{r_2}}_{120}$. However, since $R^{\hat{r_2}}_{120} = R^{k'}_{-180}R^{\hat{r_1}}_{120}R^{k'}_{180,}$ this operator does not introduce new constraints. Therefore the above three are sufficient to specify the constraints arising from symmetry.

In the case of an atom with four valence electrons (the degrees of freedom of the core is neglected) , an eigenstate can be in general expanded as

$$\Psi = \sum_i F^{L\Pi\lambda}_{Mi}(1234)\chi^{\tilde{\lambda}}_i \tag{5}$$

Where, L is the total orbital angular momentum, Π is the parity, λ denotes a representation of the S_4 group, i labels a basis function of the λ-representation, M is the Z-component of L. $F^{L\Pi\lambda}_{Mi}(1234)$ is a function of the spatial coordinates. $\tilde{\lambda}$ is the conjugate representation of λ , $\chi^{\tilde{\lambda}}_i$ is a basis function of the $\tilde{\lambda}$ $-$representation in spin space. It is well known that λ is determined by the total spin S of the atom, we have $\lambda = \{2,2\}$ if S=0, $\lambda = \{2,1,1\}$ if S=1, or $\lambda = \{1^4\}$ if S=2.

From the i' and k' axis, one can define a body frame i'-j'-k'. In this frame the spatial function can be expanded as

$$F^{L\Pi\lambda}_{Mi}(1234) = \sum_Q D^L_{QM}(-\gamma,-\beta,-\alpha)F^{L\Pi\lambda}_{Qi}(1'2'3'4') \tag{6}$$

where D^L_{QM} is the Wigner function of rotation, $\alpha\beta\gamma$ are the Euler angles for the collective rotation, Q is the component of L along the k' axis, (1234) and (1'2'3'4') denote the coordinates relative to a fixed frame and to the body frame, respectively. Owing to the transformation property inhering in $F^{L\Pi\lambda}_{Qi}$, associated with (2) to (4) there are three sets of homogeneous linear equations that the $F^{L\Pi\lambda}_{Qi}$ have to obey at ETH configurations. They read

$$\sum_{i'} \Pi e^{-i\frac{\pi}{2}Q} G^{\lambda}_{i,i'}(p(1423))F^{L\Pi\lambda}_{Qi'}(ETH) = F^{L\Pi\lambda}_{Qi}(ETH) \tag{7a}$$

$$\sum_{i'} \Pi(-1)^L G^{\lambda}_{i,i'}(p_{12})F^{L\Pi\lambda}_{-Q,i'}(ETH) = F^{L\Pi\lambda}_{Qi}(ETH) \tag{7b}$$

$$\sum_{Q'i'} B_{QQ'}G^{\lambda}_{i,i'}(p(243))F^{L\Pi\lambda}_{Q'i'}(ETH) = F^{L\Pi\lambda}_{Qi}(ETH) \tag{7c}$$

where the (ETH) denotes that the coordinates of the four electrons form an ETH, $G^{\lambda}_{i,i'}$ are the matrix elements of the $\lambda-$representation known from the textbook of group theory, and

$$\begin{aligned} B_{QQ'} &= < Q'|R^{\hat{r_1}}_{120}|Q > \\ &= \sum_{Q"} D^L_{Q"Q'}(0,\theta_0,0)e^{-i\frac{2\pi}{3}Q"}D^L_{Q"Q}(0,\theta_0,0) \end{aligned} \tag{8}$$

where $\theta_0 = \arccos(\sqrt{\frac{1}{3}})$ (cf. Fig.1).

The three sets of equations as a whole depend on and only on L, Π, and λ(or S). If there is one (or more than one) set(s) of non-zero $F_{Qi}^{L\Pi\lambda}(ETH)$ (not all of them are zero) fulfilling all the three sets of equations, then we say that Ψ can access the ETH. Otherwise, Ψ is zero at any ETH configuration disregarding the size and orientation of the ETH. In this case an INS emerges, and the ETH can not be accessed. At an ETH, when Ψ is non-zero, from (5) and (6) it can in general be written as

$$\Psi(ETH) = C \sum_{Qi} b_{Qi}^{L\Pi\lambda} D_{QM}^{L}(-\gamma, -\beta, -\alpha)\tilde{\chi_i^{\lambda}} \qquad (9)$$

Where the coefficient $b_{Qi}^{L\Pi\lambda}$ is proportional to $F_{Qi}^{L\Pi\lambda}(ETH)$. Their values are obtained by solving the equations (7a) to (7c), thus depend on L,Π, and λ but absolutely not affected by dynamics, therefore they are model-independent. Only the coefficient C as a common constant is left to be determined by dynamics. This fact reveals the decisive effect of symmetry on the eigenwavefunctions. Evidently, our discussion is quite global and not only confined in atomic systems. Owing to (7c), different Q-components are mixed up in (9). Therefore, for the states dominated by ETH-structure (the wavefunction is mainly distributed around an ETH), Q is far from an approximately conserved quantum number.

It is noted that when an ETH is deformed, the geometric symmetry becomes weaker, accordingly the constraints becomes fewer. For example, when an ETH is prolonged along one of its 2-fold axis, say, along k', the prolonged-ETH is invariant to O_a and O_b , but not O_c. Thus, instead of three sets of equations, the wavefunction at a prolonged-ETH fulfills only (7.a) and (7.b), but not (7.c). For some cases of L,Π, and λ , it was found that not only the common non-zero solutions of (7a) to (7c) do not exist, but also the common non-zero solutions of only (7a) and (7b) do not exist. In this case the INS located at the ETH will extend to the prolonged-ETH. Since an ETH has many ways to deform, the INS located at the ETH has many possibilities to extend. This fact implies that the ETH may be a source where the INS emerges and extend to its neighborhood. In other words, in a broad region surrounding the ETH, specific inherent nodal structures may pour out from the source at the ETH. Accordingly, the wavefunctions in this broad domain would be seriously affected. Nonetheless, once a wavefunction can access the ETH, it definitely can access the neighborhood of the ETH, therefore an ETH-accessible wavefunction is inherent-nodeless in the broad domain surrounding the ETH.

Another possible source of INS is located at the coplanar squares (the four electrons form a square and are coplanar with the nucleus). Let k' be normal to the plane of the square, let electrons 1 and 2 be located at the two ends of a diagonal, and let i' be parallel to $\vec{r_2} - \vec{r_1}$ as before. Then the coplanar square is invariant to

$$O'_a = PR_{180}^{k'} \qquad (10a)$$

$$O'_b = p(1324)R_{90}^{k'} \qquad (10b)$$

$$O'_c = p_{34}R_{180}^{i'} \qquad (10c)$$

Thus the $F_{Qi}^{L\Pi\lambda}$ are also constrained at the coplanar squares by three sets of equations, thereby the accessibility of the coplanar squares can be identified. As before, the accessibility depends on L,Π, and λ (or S). It is noted that the rotation operators in eq.(10) do not mix up the $F_{Qi}^{L\Pi\lambda}$ and $F_{Q'i}^{L\Pi\lambda}$with $|Q| \neq |Q'|$, but only those with the same |Q| (refer to (10c)). Therefore, at a coplanar square, an eigenwavefunction can be in general written as

$$\Psi(coplanar - square) = \sum_{|Q|} \Psi_{|Q|},$$

$$\Psi_{|Q|} = C_{|Q|} \sum_i [D_{QM}^L(-\gamma, -\beta, -\alpha) + d_{|Q|,i}^{L\Pi\lambda} D_{-Q,M}^L(-\gamma, -\beta, -\alpha)]\tilde{\chi_i^\lambda} \quad (11)$$

For a given |Q|, non-zero solutions of eq.(10) may not exist; in this case we have $\Psi_{|Q|} = 0$. Alternatively, for a given |Q|, if a non-zero solution exists, the eq.(10) as homogeneous equations can determine only the $d_{|Q|,i}^{L\Pi\lambda}$, but not the $C_{|Q|}$. When more than one non-zero $\Psi_{|Q|}$ are contained in $\Psi(coplanar - square)$, the $C_{|Q|}$ of them are all determined by dynamics. In this case, these non-zero coefficients $C_{|Q|}$ may be optimized to lower the energy.

For the intrashell states (in these states the 4-valence-electron stay in the same shell), obviously if the electrons form an ETH the Coulomb repulsion will be minimized. The other favourable configuration is just the coplanar square (in some cases the coplanar square is even better than the ETH, because the moment of inertia of a coplanar square may be larger resulting in having a smaller collective rotation energy E_{rot}). In general, the wavefunctions of all the low-lying states are mainly distributed in the domains where the total potential energy is relatively lower. Therefore, the domains surrounding the ETH and the coplanar squares are very important to the low-lying states, and the accessibility of these two domains will be crucial to the low-lying spectrum. Since the search of solutions of homogeneous linear equations is trivial, we shall neglect the details but give directly the accessibility in Table 1.

From Table 1 the $^{2S+1}L^\Pi$ states can be classified into three types as listed in the first column of Table 2. The first type can access both the ETH and the coplanar squares, these states are essentially inherent nodeless. The second type contains an INS located either at the ETH or at the coplanar squares. The third type contains INS both at the ETH and at the coplanar squares. Let an eigenenergy be divided as a sum of the internal energy E_{int} and the collective rotation energy E_{rot}. Let the lowest state of a $^{2S+1}L^\Pi$ series be called a first-state. Evidently, the more the nodal surfaces are contained, the higher the energy. As a first-state, it will contain the nodal surfaces as least as possible. If they contain any nodal surface, it was found in [6] that they would contain only the INS. Thus, we predict that the E_{int} of the first-states of the first type should be the lowest, in these states the wavefunction can be freely distributed in the most important domains without nodal surfaces, and therefore can be optimized to lower the energy. On the other hand, the E_{int} of the first-states of the third type should be considerably higher due to containing more nodal surfaces.

From the classification, the low-lying spectrum can be predicted as follows. For

L=0 states, the ${}^1S^e$ and ${}^5S^o$ states would be the lowest two (because they belong to the second type, while the other L=0 states belong to the third type). For L=1 states, the ${}^3P^e$ of the first type would be the lowest, the ${}^3P^o$ of the second type would be the second lowest. For L=2 states, the ${}^1D^e$ and ${}^3D^o$ of the first type would be the lowest two. It is noted that the wavefunctions of a Coulombic system are usually broadly distributed in the coordinate space due to the long-range character of the Coulomb force. It is also noted that the domain of the ETH and the domain of the coplanar square are closely connected (e.g., when an ETH is flattened along one of its 2-fold axis, it will become to a coplanar square). Therefore the wave functions of the first-state of the first type are expected to be smoothly distributed in both domains. This presumption was actually found in [9] (refer to Fig. 6a of [9]).

It is noted that in general the orientation of a coplanar structure (relative to L) is crucial to E_{rot}. When the normal of the coplanar structure k' is parallel to L, the moment of inertia is larger ,and therefore E_{rot} is smaller. Consequently, when a coplanar structure exists in a $F_{Qi}^{L\Pi\lambda}$ component, the larger the $|Q|$, the smaller the E_{rot}. For the ${}^3D^o$ state, a coplanar square can exist only in $|Q|$=1 component (cf. Table 1). However, for the ${}^1D^e$ state, the coplanar square can exist both in $|Q| = 2$ and 0 components. It is noted that a first-state will do its best to lower the energy. Thus the ${}^1D^e$ first-state will be dominated by the |Q|=2 component to reduce the E_{rot}. For this reason, although both the ${}^1D^e$ and ${}^3D^o$ would have favourable internal structure, we predict that the ${}^1D^e$ would be lower than the ${}^3D^o$ due to having a smaller E_{rot}. The second lowest two L=2 states would be the ${}^1D^o$ and ${}^5D^e$ of the second type. For L=3 states, all the ${}^3F^e$, ${}^5F^e$ and ${}^3F^o$ belong to the first type. However, the coplanar square can exist in $|Q| = 3$ component in ${}^3F^o$, exists only in $|Q| = 2$ component in ${}^5F^e$ and exists only in Q=0 component in ${}^3F^e$. Thus we predict that the ${}^3F^o$ is the lowest, the ${}^5F^e$ is the second lowest, while the ${}^3F^e$ is the third lowest. The ${}^1F^e$ is the fourth lowest due to belonging to the second type.

In particular, since the internal structure of the first-states of the first type is most favorable, since among all the states of the first type the ${}^3P^e$ is the one having the smallest L (therefore the smallest E_{rot}), thus we predict that the ${}^3P^e$ is the ground state. The prediction on the ordering of the first-states with their quantum numbers is given in Table 2. For the second-states, they are more energetic and therefore can access a much broader region, including the region with a higher total potential energy. Besides the INS, they will contain additional nodal surfaces because they have to be orthogonal to the first-states. We shall not discuss them in this paper.

From the above analysis, the first-states of the same type would have similar internal structures, the energy differences between them arise mainly from E_{rot}. Thus, rotation bands would exist in the spectrum, this is an important feature. The first-states of the first type including the ${}^3P^e$,${}^1D^e$,${}^3D^o$,${}^3F^o$,${}^5F^e$,${}^3F^e$,$\cdots$ would form a band headed by the ground state ${}^3P^e$, therefore this band may be called the ground-band. The internal wavefunctions $F_{Qi}^{L\Pi\lambda}$ of this band are broadly

and smoothly distributed around the ETH and the coplanar squares without nodal surface. The first-states of the second type will form two bands. One is composed of the coplanar square-accessible but ETH-inaccessible states including the ${}^1S^e$,${}^3P^o$,${}^5D^e$,${}^1F^e, \cdots$. For these states, there is a source of INS located at the ETH. Therefore their wave functions may prefer coplanar structure to avoid the INS, they are expected to be distributed smoothly around a coplanar square. This band may be called the coplanar square-band. The other band is composed of the ETH-accessible but coplanar square-inaccessible states including the ${}^5S^o$, ${}^1D^o, \cdots\cdot$. Their wave functions are expected to be distributed around the ETH. For these states, the INS at the coplanar square will spoil the stability of the ETH. In fact, a specific mode of internal oscillation induced by the INS was found in [10]. Therefore, this band may be called the ETH*-band, where the * implies that an internal oscillation with one node is inhering. There may be other higher bands, e.g., composed of the first-states of the third type. However, the above three bands are the most important bands, we shall not discuss the other possible higher bands in this paper.

At present both the experimental and theoretical results are not sufficient to check all the above predictions. Nonetheless, the data derived from an analysis of the experimental optical spectra by Moore [11] are very valuable, which are listed in Table 3 for the n=2 intrashell states of different species. Not all the ${}^{2S+1}L^{\Pi}$ symmetries are allowed for a given shell (due to the limitation in the partial wave of individual electron and due to the Pauli Principle). However, the optical data for all the allowed n=2 intrashell states are complete in the case of the ion O^{++}. These data confirm the predictions very well . The ordering of levels is exactly as predicted without an exception. Furthermore, experimentally the ground states of all the 4-valence-electron systems are a ${}^3P^e$ state just as predicted without an exception. Nonetheless, since the existing data are not complete, more data on quadruply excited states (in particular those for intrashell states with a larger n) are needed to justify the predictions.

Owing to the difficulty in calculation, the theoretical literatures on the quadruply excited states are very few. In 1994 Komninos and Nicolaides have calculated the intrashell quadruply excited ${}^5S^o$ states of Be atom by using the multiconfigurational Hartree-Fock method [12]. They found that in the first-states of the ${}^5S^o$ symmetry, the angle between the two position vectors of any two valence electrons tends to 106°. On the other hand, the angle is 109.4° for an ETH. Thus their finding supports that the ${}^5S^o$ states are dominated by the ETH-structure. In a calculation based on a r-frozen model [10] the ETH-structure of the ${}^5S^o$ states was also found. Besides, the expected INS existing at coplanar squares was confirmed in [10] (refer to Fig.6a of [10]).

In fact, the distribution of a wavefunction in coordinate space is determined by two factors, namely the total potential energy and the inherent nodal structure. Since the first factor is easier to be recognized, the second factor is crucial. In this paper, the decisive effect of the inherent nodal structure has been demonstrated, a primary classification scheme has been proposed, thereby the low-lying

spectrum can be systematically understood. Owing to the rapid progress in experimental techniques, much more data on the quadruply excited states is expected to be coming. The qualitative knowledge derived in this paper will be helpful to understand the coming data.

The generalization of the above procedure to any few-body system is straight forward. In any case, the sources of INS should be identified, a classification scheme can be established based on the understanding of the inherent nodal structure. The existence of the inherent nodal structure is a great marvel of quantum mechanics. Since different systems are constrained by symmetry in a similar way, similarity should exist and we can understand them via an unified point of view.

REFERENCES

1, T.D.Lee and C.N.Yang,Phys.Rev., 104 (1956) 254

2, F.A.Kaempffer, "Concepts in Quantum Mechanics", Acaddemic Pres, 1957

3, J.P.Elliott and P.G.Dawber, "Symmetry in Physics", Vol.1 and 2,MacMillan Press LTD.,1979

4, W.Greiner and G.E.Brown, "Symmetry in Quantum Mechanics", Springer-Verlag, 1993

5, T.Rosen, "Symmetry in Science", Springer-Verlag, 1997

6, C.G.Bao,Few-Body Systems,**13**,41,1992; Chinese Phys. Lett. 14 (1997) 20; Phys. Rev. Lett 79 (1997) 3475.

7, W.Y.Ruan and C.G.Bao, Few-Body Systems 14 (1993) 25

8, C.G.Bao, X.Z.Yang, and C.D.Lin, Phys. Rev. A55 (1997) 4168.

9, C.G.Bao J. Phys. B (At. Mol. Opt. Phys.) 26 (1993) 4671

10, C.G.Bao, Phys.Rev. A47 (1993) 1752;

11, C.E.Moore, Atomic Energy Levels, NBS Circular 467 ,1971

12, Y.Komninos and C.A.Nicolaides. Pyhs. Rev. A50 (1994) 3782

Table 1 The accessibility of favorable shapes to the $^{2S+1}L^{\Pi}$ states. An empty block implies that the corresponding state can access the ETH shape. The numbers in the blocks are the $|Q|$ of the non-zero $\Psi_{|Q|}$, in which the coplanar square can be accessed (e.g., for the $^1D^e$, both the $|Q| = 0$ and 2 components are allowed to access the coplanar squares). A block with a $\times$ implies that the state can not access the corresponding shape (e.g., the $^3D^e$ can not access both the ETH and the coplanar square).

	$^1S^e$	$^3S^e$	$^5S^e$	$^1S^o$	$^3S^o$	$^5S^o$
ETH	×	×	×	×	×	
coplanar square	0	×	×	×	×	×
	$^1P^e$	$^3P^e$	$^5P^e$	$^1P^o$	$^3P^o$	$^5P^o$
ETH	×		×	×	×	×
coplanar square	×	0	×	×	1	×
	$^1D^e$	$^3D^e$	$^5D^e$	$^1D^o$	$^3D^o$	$^5D^o$
ETH		×	×			×
coplanar square	0,2	×	2	×	1	×
	$^1F^e$	$^3F^e$	$^5F^e$	$^1F^o$	$^3F^o$	$^5F^o$
ETH	×			×		×
coplanar square	2	0	2	×	1,3	×

Table 2 A classification and the predicted ordering of levels of the intrashell first-states based on symmetry consideration. For all the states with the same L, the states in a higher row is anticipated to be lower in energy.

TYPE	$^{2S+1}L^{\Pi}$
2	$^1S^e$,$^5S^o$
3	$^3S^e$,$^5S^e$,$^1S^o$,$^3S^o$
1	$^3P^e$
2	$^3P^o$
3	$^1P^e$,$^5P^e$,$^1P^o$,$^5P^o$
1	$^1D^e$
1	$^3D^o$
2	$^5D^e$,$^1D^o$
3	$^3D^e$,$^5D^o$
1	$^3F^o$
1	$^5F^e$
1	$^3F^e$
2	$^1F^e$
3	$^1F^o$,$^5F^o$

Table 3 The energies (in cm^{-1}) of the n=2 intrashell states of 4-valence-electron atomic systems given by Moore [11]. The energy of the ground state $^3P^e$ is zero . All the n=2 intrashell states allowed by the Pauli Principle are listed . The label $^1S^e(2)$ denotes a second-state, etc.

TYPE	$^{2S+1}L^{\Pi}$	C	N^{+}	O^{++}
2	$^{1}S^{e}$	21648	32687	43184
2	$^{5}S^{o}$	33735	47168	60312
3	$^{3}S^{o}$		155130	197086
	$^{1}S^{e}(2)$			343302
1	$^{3}P^{e}$	0	0	0
2	$^{3}P^{o}$	75256	109218	142382
3	$^{1}P^{o}$		166766	210458
	$^{3}P^{e}(2)$			283759
1	$^{1}D^{e}$	10194	15316	20271
1	$^{3}D^{o}$	64089	92238	120025
2	$^{1}D^{o}$		144189	187049
	$^{1}D^{e}(2)$			298289